

ELECTROCHEMICAL TESTING OF PASSIVITY STATE AND CORROSION RESISTANCE OF SUPERMARTENSITIC STAINLESS STEELS

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On low interstitial - supermartensitic stainless steels (X1CrNiMo 12-5-1, X2CrNiMo 13-6-2, X1CrNiMo 12-6-2) the electrochemical potentiodynamic polarization tests were carried out and the passive state stability and localized corrosion resistance were compared and evaluated. The effect of quenching and tempering as well as the changes in microstructure on polarisation curves and corrosion properties at room temperature were established. Small differences in chemical composition of steels were also registered on their corrosion parameters changes and resistance.

Key words: martensitic stainless steel, heat treatment, polarization test, corrosion properties

Elektrokemijsko ispitivanje stabilnosti pasivnog stanja i korozijske otpornosti supermartenzitnog nehrđajućeg čelika. Rad prikazuje usporedbu i procjenu stabilnosti pasivnog stanja i lokalnu otpornost koroziji temeljem ispitivanja elektrokemijske potenciodinamičke polarizacije nisko-intersticijskih supermartenzitnih nehrđajućih čelika (X1CrNiMo 12-5-1, X2CrNiMo 13-6-2, X1CrNiMo 12-6-2). Utvrđeni su utjecaj poboljšavanja čelika i mikrostrukturne promjene na polarizacijskim krivuljama uzoraka te korozijska svojstva pri sobnoj temperaturi. Uočena je i povezanost malih odstupanja kemijskog sastava čelika s promjenom korozijskih parametara i korozijskom otpornošću.

Ključne riječi: nehrđajući martenzitni čelik, toplinska obrada, polarizacijsko ispitivanje, korozijska svojstva

INTRODUCTION

Low interstitial high alloyed martensitic stainless steels (supermartensitic, SMSS) with higher values of strength properties, good weldability and reasonable corrosion resistance are used mainly in the oil and gas industry, flow lines, offshore structures and they are perspective in other branches (chemistry, transport). Considerable attention has been devoted to stress corrosion cracking in hydrogen or H₂S containing environments [1].

Classical martensitic stainless steels (0,1 – 1 % C, 12 – 18 % Cr, Mo < 1,5 %) have a lower corrosion resistance in comparison with other groups of stainless steels. Supermartensitic stainless steels were developed from the original “COR” martensites (X5CrNiMo 13-4) [2] with reduced content of interstitial elements C + N to 0,01 %.

The corrosion resistance of super-martensitic steels is between martensitic and duplex stainless steels (X2CrNi 23-4). The super-martensitic steel can replace more expensive duplex or austenite stainless steels in some environments.

Supermartensitic steels have good corrosion resistance in CO₂ containing water solutions. Three types of supermartensitic steels are used: a) lean alloy: 10 – 12 % Cr and 2,5 % Ni, b) medium alloy: 11 – 13 % Cr, 4 – 5 % Ni, 1 – 2 % Mo, d) high alloy 11 – 13 % Cr, 6 – 7 % Ni, 2 – 3 % Mo (recommended for CO₂ containing environment with small amount of H₂S). Some SMSS contain addition of Cu < 1,5 %, N < 0,1 %, and small amounts of Al, Co, Nb, V. Metallurgy of SMSS is controlled by requirement that structure at all cooling rates would be martensitic without δ ferrite.

The aim of this contribution was to investigate passive state stability and pitting corrosion resistance of stainless steels X1CrNiMo 12-5-1, X2CrNiMo 13-6-2 and X1CrNiMo 12-6-2 after quenching and tempering on the basis of standard potentiodynamic polarization tests. These tests are useful for assessment of heat treatment and structure influence on corrosion properties.

TESTED STAINLESS STEELS

The chemical composition of the steels is given in Table 1, where the values of pitting resistance equivalent PRE = (Cr)+3,3(Mo)+16(N) (wt. %) are also calculated. The control microanalysis was performed on the device JEOL JSM6490 LV.

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Table 1. Composition of tested steels

steel	X1CrNiMo	X1CrNiMo	X2CrNiMo
w _W /%	12-5-1	12-6-2	13-6-2
C	0,014	0,011	0,017
Mn	1,03	0,56	0,55
Si	0,38	0,30	0,30
P	0,024	0,026	0,030
S	0,003	0,001	0,001
Cr	11,65	12,36	12,98
Ni	4,73	6,22	6,15
Mo	1,42	2,33	2,37
Al	0,001	0,02	0,001
N	0,012	0,011	0,010
Ti	-	0,10	0,10
Cu	0,25	0,15	-
PRE	16,5	20,2	20,9

Heat treatment can influence significantly the mechanical properties and corrosion resistance of supermartensitic steels. The quenching of steels consisted of heating up to 970 °C, holding time 1,0 hour and cooling in air. After quenching the one half of samples were tempered at 600 °C/6 h/air. The metallographic observations of structure were performed on the as-received, quenched and tempered steels (Figures 1-3).



Figure 1. Microstructure of quenched steel X2CrNiMo 13-6-2

In the quenched state were observed fine martensite structure and small amount of retained austenite.

After tempering the reverse austenite (20 - 22 %) was detected by X-ray diffraction. In stainless steel X1CrNiMo 12-5-1, δ -ferrite was also observed that can influence mechanical and corrosion properties [1, 3].

The specimens for electrochemical corrosion tests were made of tubes $\varnothing 200 \times 20$ mm or thick plates, their exposed surfaces were finished by fine SiC paper (up to no. 1200), wet grinding and cleaning.

Passive state stability and resistance to pitting has been tested by the standard method [4], which is applied

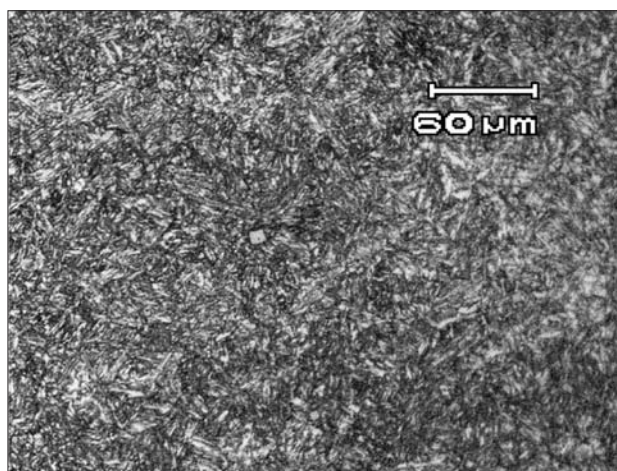
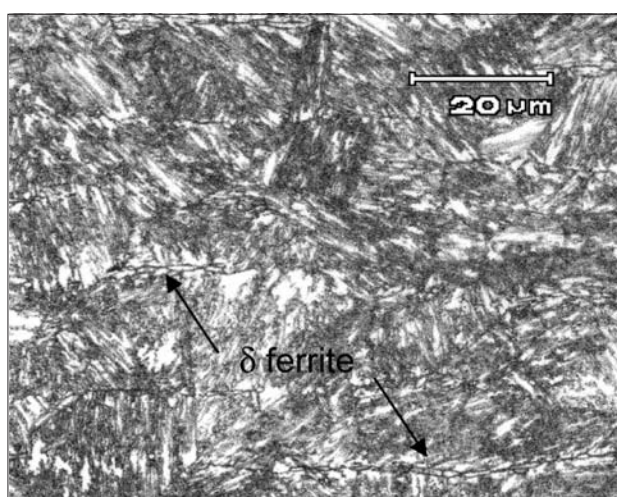


Figure 2. Tempered steel X2CrNiMo13-6-2 micro-structure

Figure 3. Microstructure of tempered steel X1CrNiMo 12-5-1 with δ ferrite

for stainless steels. Inside pits as stress concentrators a solution is more acid and aggressive that can initiate stress corrosion cracking or fatigue.

The potentiokinetic (potentiodynamic) polarization reactivation method has been developed for testing and evaluation of intergranular corrosion sensitivity as well as stability of passive state [5].

Polarization methods for pitting and/or intergranular corrosion and passive state stability of stainless steels were used also in the works [6-8].

RESULTS AND DISCUSSION

Potentiodynamic cyclic measurements of pitting resistance were carried out according to standard [4] using potentiostat PGP201 and a special corrosion cell with 1,0 mol/l NaCl water solution at room temperature. The exposed area 0,5 - 1 cm² and polarization rate 0,3 mV/s were set up. Potential was measured by saturated calomel electrode (SCE).

Examples of potentiodynamic polarization curves (loops) are documented in Figure 4 and further results of pitting are compared in Table 2.

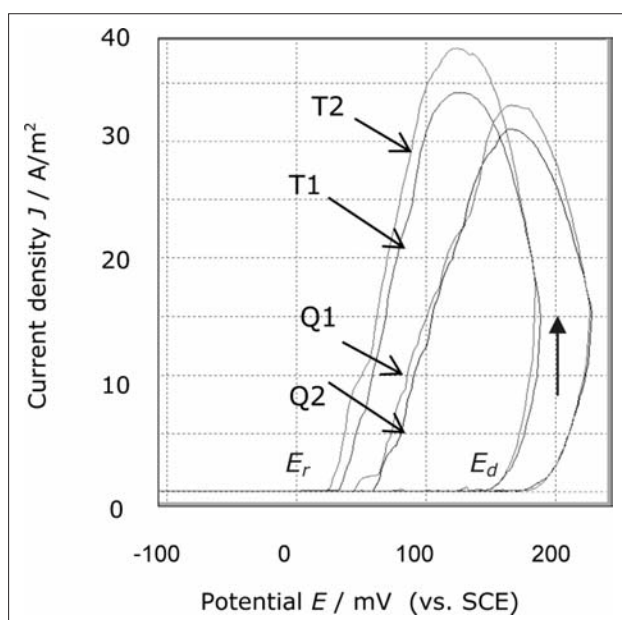


Figure 4. Potentiodynamic polarization curves of pitting. Steel X1CrNiMo 12-6-2 after quenching (Q) and tempering (T). The first (1) and second (2) cycles. Depassivation (E_d) and repassivation (E_r) potentials

A higher resistance to pitting is characterized by higher values of depassivation (E_d , at $J = 1,0 \text{ A/m}^2$) and repassivation (E_r , at $J = 0,1 \text{ A/m}^2$) potentials. The corrosion potential (E_{cor} , $J = 0$) and differences ($E_d - E_{cor}$) or ($E_r - E_{cor}$) must also be considered under given conditions.

The results (Table 2) have shown a better resistance of quenched (Q) steels to pitting in comparison with tempered (T) ones and higher values of pitting potentials (E_d , E_r) for steels with 2,3 % Mo. This is explained by chromium carbide formation and Cr depletion of matrix. In summary the tested stainless steels (Table 1) have similar resistance to pitting in water chloride solution as commercial austenitic steel CrNi.18-10. Pitting resistance equivalent (PRE ≈ 20) has nearly equal values for both steel types.

Table 2. Results of pitting corrosion test

steel	heat treat.	E_d	E_r	E_{cor}	cycle
		mV	mV	mV	
X1 CrNiMo 12-5-1	Q	178	18	-156	1
		167	0	-168	2
	T	160	-16	-134	1
		110	-50	-166	2
X1 CrNiMo 12-6-2	Q	163	54	-153	1
		132	75	-151	2
	T	147	13	-219	1
		120	2	-106	2
X2 CrNiMo 13-6-2	Q	176	42	-99	1
		172	56	-103	2
	T	143	23	-103	1
		137	32	-114	2

On the basis of potentiodynamic polarization curves in large potential range (Figure 5) the parameters related to the passive state of quenched (Q) and tempered (T) steels were determined, see Table 3: critical passivation potential (E_p), critical passivation current density (J_p), minimal current density in passive state (J_{pmin}) and transpassive potential (E_t). The difference ($E_t - E_p$) as the range of passive area can be also calculated.

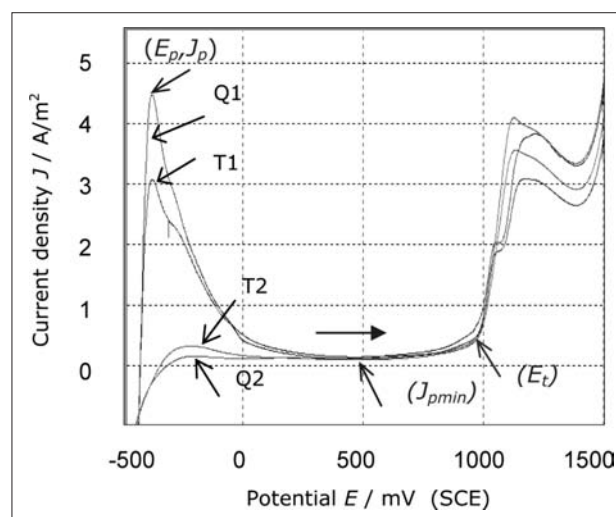


Figure 5. Polarization curves of steel X1CrNiMo12-5-1, quenched (Q) or tempered (T) state. Testing in water solution 0,5 mol/l H_2SO_4 , 25 °C, first and second cycles (1,2)

On the basis of this test the relatively small differences were found out in the stated parameters according to chemical composition and/or heat treatment. For example the passive area width is approximately 1,1 V for steels X2CrNiMo 13-6-2 and X1CrNiMo 12-6-2 and/or 0,98 V for steel X1CrNiMo 12-5-1.

Table 3. Results of potentiodynamic polarization test of steels

steel	heat treat.	E_p	J_p	J_{pmin}	E_t
		mV	$\mu\text{A/cm}^2$	$\mu\text{A/cm}^2$	
X1 CrNiMo 12-5-1	Q	-378	446	11,9	941
		-202	13,7	8,9	935
	T	-379	305	8,7	952
		-218	30,7	7,3	915
X1 CrNiMo 12-6-2	Q	-350	100	12,0	950
		-231	11,3	4,8	990
	T	-237	137	11,0	980
		-220	17	6,9	998
X2 CrNiMo 13-6-2	Q	-341	117	11,2	952
		-200	16,7	7,6	938
	T	-327	91,2	10,8	956
		-197	11,2	7,6	936

Significant lower values of current density in the active state (J_p) in the second cycles can be explained by

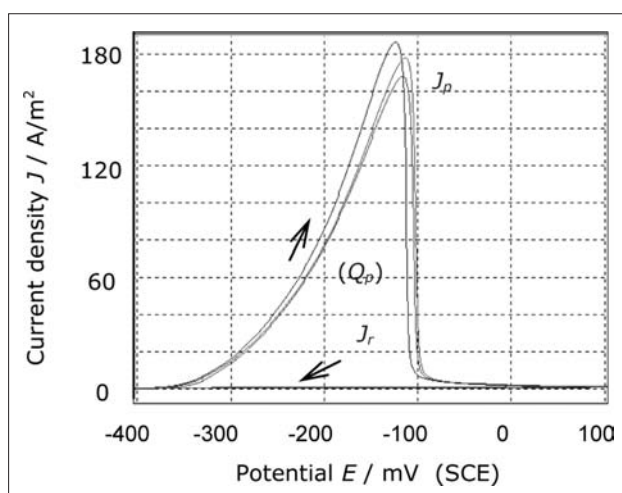


Figure 6. Quenched steel X1CrNiMo12-6-2. Potentiokinetic reactivation test (EPR, three cycles, see Table 4)

passivation during first cycle. This outlines the possibility of electrochemical passivation of tested steel in certain solutions.

By means of electrochemical potentiokinetic reactivation (EPR) method [5] the resistance to localized (intergranular, interphase) corrosion was tested in standard water solution 0,5 mol/l $H_2SO_4 + 0,01$ mol/l KSCN. On quenched steels X2CrNiMo 13-6-2 and X1CrNiMo 12-6-2 the higher stability of passive state to localized corrosion were found out in comparison with state after tempering, Figure 6 and 7.

These tempered steels have shown increased values of reactivation ratios of current and/or charges as consequence of dissolution of chromium depleted local areas. The recorded double current peak is consequence of different rate of dissolution of austenite and martensite in the active state, Figure 7. Austenite area contains more nickel and related peak is shifted to higher potential values.

In Table 4 the results of EPR method are compared for tested steels and heat treatments. The steel is resistant to localized (intergranular, interphase) corrosion if values of reactivation ratios J_r/J_p are smaller than 1%, slight sensitivity corresponds to values J_r/J_p in the range 1-5 % and steel is sensitive to this corrosion at $J_r/J_p > 5$ % [5].

The steel X1CrNiMo 12-5-1 (lower contents of Cr, Mo, Ni) has much higher values of anodic current density peak and reactivation ratios than other tested steels, Table 4.

The higher are values of reactivation ratios J_r/J_p or Q_r/Q_p , the smaller is the stability of passive state and corrosion resistance. Values of electric charges Q_p and Q_r , passing through unit of exposed surface, are proportional to the area under corresponding peaks ($Q = \int J(t) dt$, where t - time).

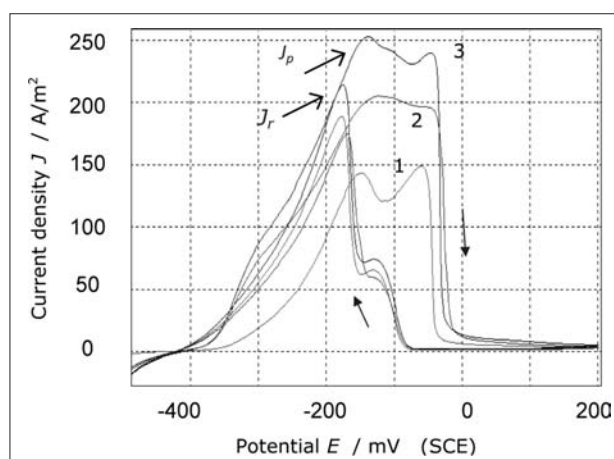


Figure 7. Polarization curves of tempered stainless steel X1CrNiMo 12-6-2. Standard solution, 3 cycles

Table 4. EPR test results. Passivation (J_p) and reactivation (J_r) current density or reactivation ratios (J_r/J_p or Q_r/Q_p). Heat treatment : Q – quenching, T – tempering

steel	heat treat.	J_p	J_r	J_r/J_p	Q_r/Q_p
		mA/cm ²		%	%
X1 CrNiMo 12-5-1	Q	38,9	12,8	32,9	30,9
		42,2	15,0	35,5	33,4
		38,8	14,1	36,5	30,8
	T	34,4	31,8	92,3	76,7
		42,1	36,8	87,3	60,1
		44,4	37,2	83,8	59,0
X1 CrNiMo 12-6-2	Q	18,6	0,005	0,029	0,07
		16,7	0,015	0,090	0,03
		17,7	0,031	0,173	0,45
	T	14,8	18,8	126,8	88,2
		20,5	17,4	85,1	46,3
		25,2	21,3	84,6	47,7
X2 CrNiMo 13-6-2	Q	15,7	0,1	0,636	0,97
		14,1	0,05	0,354	0,46
		15,7	0,07	0,446	0,23
	T	22,8	23,6	103,2	78,0
		27,3	22,8	83,6	50,9
		32,2	28,4	88,3	55,5

CONCLUSION

Corrosion electrochemical standard tests of supermartensitic stainless steel X1CrNiMo 12-5-1, X1CrNiMo 12-6-2 and X2CrNiMo 13-6-2 carried out in this work justified the conclusions:

The small differences in chemical composition of steels were detected as relatively small changes in electrochemical characteristics and parameters of pitting corrosion as well as passive state stability.

These steels after tempering (600 °C/6 h/air) have lower corrosion resistance in comparison with quenched

states. This difference is explained by higher heterogeneity of structure and changes of chemical composition in tempered state.

The most sensitive method for detection of chemical and/or structural changes of investigated steels is electrochemical potentiokinetic reactivation (EPR) method. Higher differences in corrosion parameters of steels were measured by this method.

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